STATUS REPORT

PROFILE MODIFICATION AND IMPROVED SWEEP EFFICIENCY USING ALCOHOL-INDUCED SALT PRECIPITATION WITH CO_2 GAS FLOODS

By Clarence Raible and Tao Zhu

Project BE5B, Milestone 6, FY93

DISCLAIMER

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PROFILE MODIFICATION AND IMPROVED SWEEP EFFICIENCY USING ALCOHOL-INDUCED SALT PRECIPITATION WITH CO$_2$ GAS FLOODS

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ABSTRACT

A selective plugging process based on salt precipitation was studied to improve volumetric sweep efficiency of CO$_2$ floods. This process was based on adding an alcohol to brine to reduce the solubility of the salt. The salt precipitation process used a concentrated brine preflush followed by water-soluble alcohol injection. These studies indicated the most effective agents for this process were ethanol and concentrated NaCl brine. The mixing of NaCl brine and ethanol will cause salt precipitation, reduce permeability, and partially block subsequent flow. By blocking high-permeability zones, subsequent flow will be diverted to lower permeability areas with higher oil saturation.

Several factors contribute to selective placement of concentrated brine and alcohol in high-permeability layers or thief zones. After waterflood, injected brine and alcohol will preferentially flow through waterflooded zones because of the high relative permeability to these fluids. Also, because of low fluid viscosities, viscous crossflow during brine and alcohol injection will be minimized which will result in better placement in higher permeability layers.

The salt precipitation method provides other potential advantages over other profile modification methods such as polymer gels. Salt precipitation and profile modification by this method largely are not affected by adsorption, and reservoir conditions such as pH, and temperature. The solid salt is relatively stable to subsequent CO$_2$ flooding. Carbon dioxide flooding will lower the pH of reservoir fluids, a condition which may affect the stability of some polymer gels.

Coreflooding experiments were conducted to test the effectiveness of profile modification by salt precipitation. Cores with permeabilities modified by salt precipitation were resistant to subsequent waterfloods with a low-salinity brine. After several pore volumes of low-salinity brine injection, the core permeabilities recovered only 5 to 10% of the original permeability. Other corefloods were conducted with parallel cores of high and low permeabilities. After salt precipitation treatment, the fluid production ratio between the high- and low-permeability cores was reduced, indicating fluid diversion to the low-permeability core with additional oil production. Also, for immiscible CO$_2$ floods, increased oil recovery was obtained using salt precipitation treatments.

INTRODUCTION

This project is directed to the development of methods to improve oil recovery by CO_2 flooding. Of the enhanced oil recovery methods, gas-driven processes produce nearly one-third of the current EOR production. One of the problems associated with CO_2 floods is the occurrence of early CO_2 breakthrough which results in poor volumetric sweep efficiency. Because of gas channeling, portions of the reservoir are not contacted and displaced by the gas flood which results in bypassed oil. To recover unswept oil, a technique is required to restrict or block the higher permeability channels and direct injected CO_2 into less permeable reservoir areas which normally contain significant quantities of oil.

For CO_2 floods, poor sweep efficiency is particularly critical because of the costs associated with CO_2 injection. In addition, the problems associated with gas channeling are magnified because of the high CO_2 mobility to oil and water. Low density and viscosity of the CO_2 phase contribute to poor sweep efficiency and gravity segregation. Currently, the water-alternating-gas (WAG) process is used to reduce the relative permeability of gas. Water injection only temporarily reduces gas channeling, and the basic problem remains with an unfavorable mobility ratio for gaseous CO_2.

For FY93, a new method[1] was studied for profile modification by plugging high-permeability zones. This method was based on salt precipitation resulting from the injection of concentrated brine and alcohol slugs. Mixing of alcohol and concentrated brine will cause a reduction in the salt solubility, and precipitation of solid salt in the larger pores of the permeable flow channels. The method potentially could result in the selective plugging of the more permeable flow paths and divert subsequent fluid-flow to less permeable areas with higher oil saturations to improve the sweep efficiency of CO_2 floods.

There are several advantages for the "salt precipitation" method over other profile modification techniques. Typically, polymer solutions used for profile modification have relatively high viscosities. Various authors[2-3] have shown that viscous fluid injection can result in crossflow into less permeable strata where polymer invasion can impede and block subsequent flooding processes such as CO_2 floods. Viscous crossflow will also limit the extent of polymer penetration and placement in high-permeability layers or thief zones. Processes to form polymer gels often are subject to the same limitations of viscous crossflow during injection. For the alcohol-induced salt precipitation method, the injected fluids of brine and alcohol both have low viscosities. Injection of these lower viscosity fluids will reduce viscous crossflow resulting in better penetration and more selective placement in higher permeability thief zones. In addition, brine and alcohol are miscible with connate waters which will enhance placement of these fluids in water zones with high permeabilities. There are other inherent advantages for the salt precipitation method. Polymer gelation processes often require a suitable temperature and pH to prevent crosslinker precipitation.

The reservoir pH and temperature also affect the time required for crosslinking which can result in premature gelation. These are conditions which are difficult to control in the reservoir. The temperature and pH of the reservoir and injected solutions will have little effect on the salt precipitation method. Also, after salt precipitation, the salt is a stable solid which is not affected by pH changes associated with subsequent CO_2 flooding.

PHASE BEHAVIOR STUDIES

Experimental Procedure

For mobility-control of gas flooding, a feasibility study was conducted using salt precipitation. Phase equilibrium experiments were performed to determine the quantity of salt precipitation using different alcohols and salts. Screening tests were performed to determine which alcohol would be most effective for the salt precipitation process. Ethyl alcohol used in these studies was supplied by Quantum Chemical Corporation. According to the manufacturer, the alcohol was 200 proof anhydrous ethanol containing less than 0.5 ppm benzene. The other alcohols (methanol, isopropanol, and n-butanol) were reagent grade with a purity greater than 99.9%.

Methanol and ethanol were completely miscible with saturated NaCl brines. Precipitation experiments were conducted by mixing ethanol and brine saturated with NaCl. Solutions were agitated for more than 1 week to allow for complete phase equilibration. The solutions were then filtered through a 5 μm filter, and the filtrate was evaporated to measure the quantity of dissolved salt. The quantity of salt precipitation was calculated as the difference between the salt in the initial brine and the salt remaining in solution.

Results of Phase Studies

As shown in Table 1, 1.47 g of NaCl was soluble in 100 g of methanol, whereas NaCl was only slightly soluble in ethanol. NaCl was even less soluble in isopropanol and n-propanol. Other phase studies were conducted with the alcohols and NaCl brines. Methanol and ethanol were completely miscible with brine. Although isopropanol and n-butanol were miscible with water, the alcohols separated into two phases when mixed with brines. Limited miscibility of isopropanol and butanol would limit the alcohol concentration in the brine. This also would limit the quantity of salt precipitation, and isopropanol and butanol would be less effective for salt precipitation from brines. On the basis of these phase studies, ethanol would be the most effective alcohol for precipitation of NaCl.

To determine if there was an advantage for using salts other than NaCl, alcohol solubility tests were conducted with other salts including KCl and $CaCl_2$. These salts were more soluble than NaCl in water-alcohol mixtures. Also, produced brines containing high concentrations of

TABLE 1

Solubility of NaCl in Various Alcohols at 23.5° C

	Methanol g/g	Ethanol g/g	Isopropanol g/g	n Butanol g/g
Wt of NaCl per 100 g of alcohol	1.47	0.07	0.013	<0.008

NaCl are potential sources of salt for the salt precipitation process. In addition, other salts are usually more expensive. For these reasons, only NaCl was used throughout the remainder of this study.

Figure 1 shows the results of salt precipitation at 23.9° C. The amount of NaCl dissolved per gram of water in the solvent (water and ethanol) was a linear function of the fractional water concentration of the solvent. This linear relationship allowed for the calculation of the saturated salt concentration for any water/ethanol mixture at this temperature.

Additional experiments were performed for the dissolution of NaCl in various concentrations of water and ethanol containing an excess of salt. One of the objectives of the dissolution experiments was a simplified experimental procedure for other phase studies. After allowing the solutions to equilibrate, the NaCl concentration was measured by evaporation of the filtered solution. These results at 22.5° C, shown in Fig. 2, had the same relationship as the salt precipitation experiments.

Other tests were performed at higher temperatures. Results at 49° C (Fig. 3) show the same linear relationship, although the regression slope was slightly larger because NaCl was slightly more soluble at the higher temperature. The regression intercept for these plots is meaningless as the water concentration approaches zero. At the intercept, NaCl solubility depends on the salt solubility in the alcohol. Since NaCl was virtually insoluble in ethanol (Table 1), the regression intercept was nearly zero. The NaCl solubility in ethanol mixtures can be closely approximated as product of the water concentration by weight and the saturated NaCl solubility in water at a specific temperature.

Additional dissolution tests were performed with methanol. As shown in Table 1, NaCl was more soluble in pure methanol than ethanol. Also, as shown in Fig. 4, NaCl solubility was somewhat more soluble in methanol solutions, and methanol would be less effective on a weight basis for initiating NaCl precipitation than ethanol.

These experimental results indicated that on a weight basis ethanol produced the largest quantity of salt precipitation. Methanol also could be used for salt precipitation although methanol
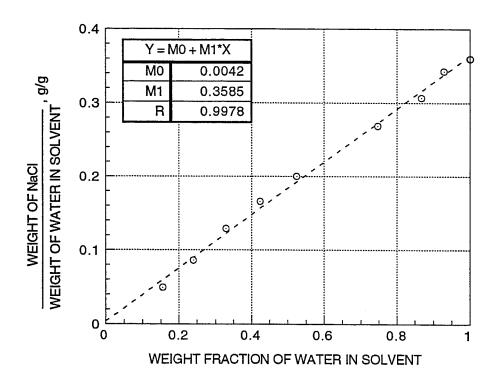
FIGURE 1. - Weight of NaCl dissolved in water/ethanol solutions after salt precipitation at 23.9° C.
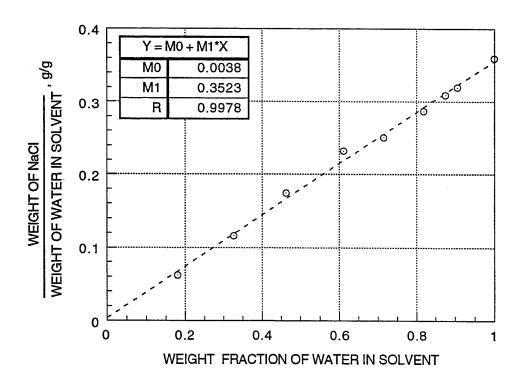

FIGURE 2. - Weight of NaCl dissolved in water/ethanol solutions by salt dissolution at 22.5° C.
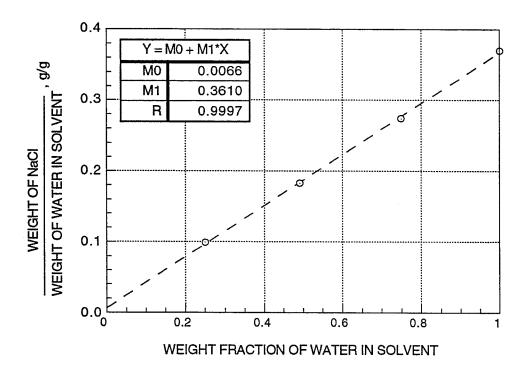
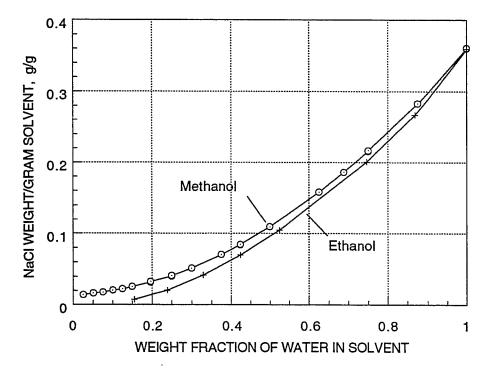FIGURE 3. - Weight of NaCl dissolved in water/ethanol solutions by salt dissolution at 49° C.

FIGURE 4. - Solubility of NaCl in water and alcohol solutions at 23.9° C.

would produce less precipitation. For field applications of the salt precipitation process, the relative cost of methanol and ethanol would be important in determining which alcohol is the most cost effective.

Particle Size of Precipitated Salt

As a mechanism for profile modification, the salt precipitation method depended upon forming salt particles to plug flow channels in the porous media. Therefore, the particle size of precipitated salt was measured after mixing NaCl-saturated brine with ethanol. Using a microscope to observe the particle sizes, different proportions of brine and ethanol were observed for mixtures ranging from 2.5 to 90% brine. The particles were distinctly cubic in shape, a characteristic of halite salt crystals. For solutions with a very low concentration of brine, many of the particles were too small to measure with a microscope. For solutions with 2.5 to 5% brine, many of the observable particles were 1 to 3 microns, and after 6 days there was little observable change in particle size.

For solutions containing 10 to 90% brine, initially after mixing brine with ethanol, there was only a small difference in particle size distributions for solutions containing different proportions of brine to alcohol. For these solutions, the smaller particles were about 2 to 5 μm in size; larger crystals ranged up to about 12 μm.

After 3 to 5 days, the mixtures were observed for changes in particle size. For solutions containing a higher proportion of brine, there was a noticeable increase in particle size with some of the larger particles increasing to 40 to 60 μm. Many of the particles exhibited different crystalline shapes other than cubic indicating further crystalline growth with time.

Several observations can be made on the effect of brine to alcohol concentration from these experiments. For solutions with very low brine concentration, crystal size was limited because there was insufficient salt present to form larger crystals and to sustain further crystal growth. At higher brine concentrations, larger crystals were formed initially and the size of the salt crystals increased with time.

COREFLOOD STUDIES

Core Properties

Coreflood tests of the profile modification method, using alcohol-induced salt precipitation, were conducted with Berea sandstone cores. The brine permeability of these cores ranged from 90 to 800 mD with a porosity ranging from 21.6 to 23.4%. Lengths of the cores were 27 to 30 cm with a diameter of 3.81 cm.

Two mercury invasion tests were performed to determine the pore throat radius of cores used in the coreflooding tests. The mercury injection samples were cut from high- and low-permeability

Berea blocks. Also, core plugs cut adjacent to the mercury samples were measured for permeability. Brine permeabilities ranged from 700 to 800 mD, and from 90 to 100 mD for the high- and low-permeability blocks. Of interest was the size of the larger pore throat radii that would control fluid flow. As shown in Fig. 5, the higher permeability sample contained a large number of pore throat radii ranging in size from 10 to 20 μm. The pore throat size peaked at about 12 μm. A broader spectrum of pore sizes was measured for the low-permeability sample. The pore entry radius of larger pores ranged in size from 2 to 12 μm with a median size of about 7 μm.

Permeability Modification Using Alcohol-Induced Salt Precipitation

Experimental Conditions

All coreflood experiments were conducted with oil-free conditions at room temperature. The cores were initially saturated with NaCl-saturated brine, and the core permeability was measured with NaCl-saturated brine. All experiments were performed with no backpressure, and the pressures across the cores were measured by a water manometer. For coreflood tests, alternating-alcohol- brine slugs were injected to initiate salt precipitation in the cores. Brine and alcohol were injected into separate injection ports in the core-piece inlet to prevent fluid mixing prior to contacting the core. Further, during the ethanol slug injection, brine was injected continuously at 25% of the ethanol injection rate to minimize plugging in the inlet section of the core. Fluids were injected at 7.5 ft/d (2.3 m/d) and each slug was about 5% PV. After ethanol injection, the core was shut-in to allow for salt precipitation. Various shut-in times were used to measure the effect of equilibrium time on permeability reduction. Then, NaCl-saturated brine was injected at 3 ft/d (0.9 m/d) to determine permeability reduction in the core.

Factors That Affect Permeability Reduction Using Salt Precipitation

Coreflood experiments were conducted to evaluate different factors to determine their effect on permeability reduction after injecting alcohol and saturated brine. These included the effect of core permeability, the size of the alcohol slug, equilibrium time, and the brine to alcohol injection ratio.

Effect of Original Core Permeability on Permeability Reduction

Permeability reduction experiments were performed to determine the effect of original core permeability after salt precipitation. Approximately 0.3 pore volume (PV) of alcohol divided into six slugs was injected into each core. Each alcohol slug (5% PV) was followed by injecting the same slug size of NaCl-saturated brine. Approximately 0.2 PV NaCl-saturated brine was injected after the last alcohol slug. Then, the cores were shut-in 64 hours for core 1, 65 hours for core 2, and 41 hours for core 3. Following the shut-in period, the brine permeability was measured with
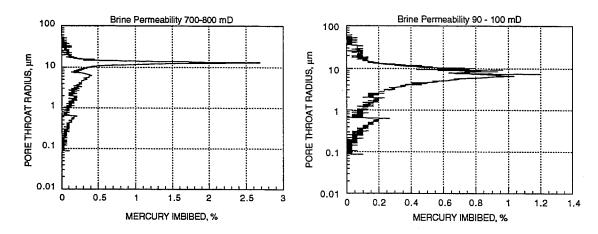
FIGURE 5. - Mercury invasion tests showing pore throat entry radii of sandstones used in coreflood experiments.

NaCl-saturated brine. The results of these three experiments are presented in Fig. 6. Following alcohol injection and the shut-in interval, the brine permeabilities were measured. Core 1 with an original permeability of 487 mD was about 10% of the original permeability, core 2 with an original permeability of 683 mD was about 20%, and core 3 with an original permeability of 786 mD was about 40%. Also, Fig. 7 shows for these and other experiments the effect of alcohol slug size with cores ranging in permeability from 450 to nearly 800 mD. Also, the experiments indicated that the original core permeability influenced the degree of permeability reduction; that is, with higher original core permeability, less permeability reduction was obtained after salt precipitation.

This effect of original core permeability on permeability reduction may be caused by the salt crystal size. Bottle test observations indicated that the majority of the salt crystals were about 2 to 5 μm when NaCl-saturated brine was mixed with ethanol for short equilibrium times. Mercury injection tests indicated a median pore throat radii of about 12 μm for the core with a permeability of about 700 mD, and about 7 μm for the core with a permeability of about 100 mD (Fig. 5). In high-permeability cores, because of the small size of salt crystals compared to the larger pore throats, the salt precipitate may only result in partial plugging of the pore throats. On the other hand, the salt precipitate may result in greater plugging of the pore throats in lower permeability cores.
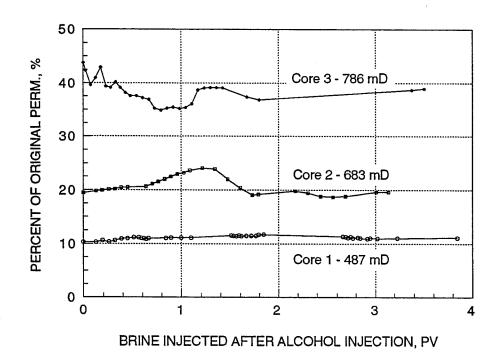
FIGURE 6. - Effect of original brine permeability. After salt precipitation, higher permeability reduction was measured with lower permeability cores.
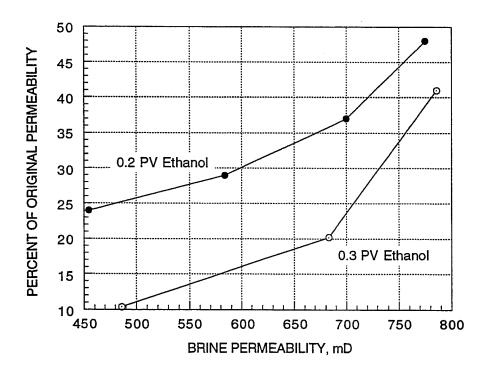
FIGURE 7. - Permeability reduction of cores after injecting NaCl-saturated brine and ethanol slugs.

Effect of Ethanol Volume on Reducing Permeability

The effect of alcohol volume on reducing permeability was conducted on several cores with about the same permeability (core 2 - 683 mD) and (core 4 - 702 mD). Figure 8 shows the effect of injecting 0.3 and 0.2 PV of ethanol. For core 4, there was a noticeable increase in permeability after 1 PV of brine injection. Solid salt was produced after 1 PV, and the increase in permeability may have been due to fine particle migration. When the ethanol slug size was compared (0.2 and 0.3 PV), the larger alcohol slug size was somewhat more effective in reducing the permeability. This was the same trend that was shown previously in Fig. 7.

Effect of Equilibrium Time on Permeability Reduction

Another factor which influenced permeability reduction was the shut-in time to allow for salt precipitation and salt crystal growth. An experiment was conducted to measure the effect of equilibrium time on permeability reduction by shutting-in the core for several time intervals after alcohol injection. Initially, the core with an initial brine permeability of 724 mD was shut-in for 65 hours and then measured for brine permeability. As shown in Fig. 9, a permeability reduction of 50% was measured. Then the core was shut-in for an additional 64 hours. After the second shut-in, the core measured about 30 % of the original permeability.
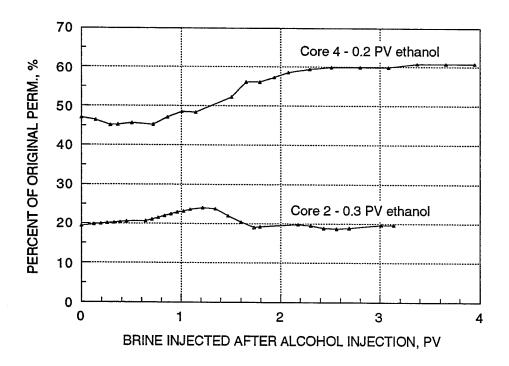

FIGURE 8. - Permeability reduction of cores after injecting 0.2 and 0.3 PV of ethanol.
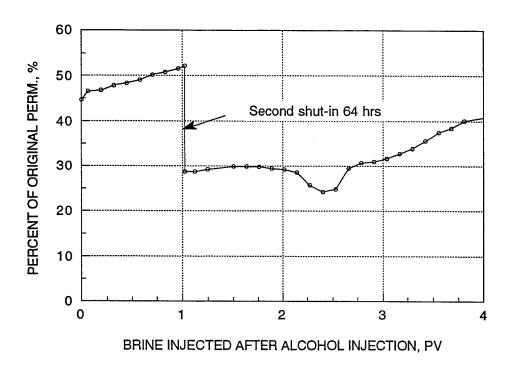
FIGURE 9. - Permeability reduction of core with increasing shut-in time.

Although sufficient information is not presently available on the optimum shut-in time necessary to achieve maximum permeability reduction, data in Fig. 10 suggested a time interval of at least 1 week was required. This trend of time dependence for increasing particle size was also observed in bottle tests.

Effect of Brine to Alcohol Injection Ratio

Another experiment was conducted to determine the effect of brine to alcohol ratio on permeability reduction. Two cores (numbers 5 and 6) with identical permeabilities of 775 mD were used for these tests. The total alcohol volume was injected as 4 slugs and alternated with saturated brine injection. For the test with core 5, the total volume of alcohol was 0.21 PV with an equal volume of saturated brine. For the test with core 6, the ratio of injected brine was double that of the alcohol. A total of 0.36 PV of saturated brine and 0.18 PV of alcohol was injected. The experimental results for these tests are plotted in Fig. 11 where the larger brine to alcohol ratio increased the degree of permeability reduction. Bottle tests also indicated that solutions containing higher proportions of brine enhanced growth of the salt crystals to a larger size.
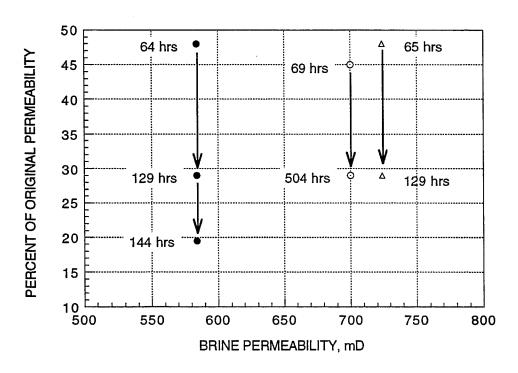
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FIGURE 10. - Permeability reduction for various shut-in times after initial injection of NaCl-saturated brine and ethanol slugs.
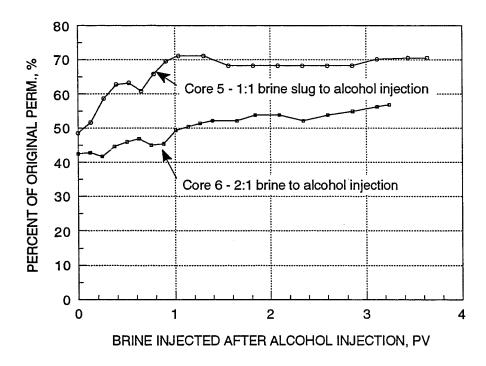

FIGURE 11. - Permeability reduction for different ratios of brine and alcohol injection.

Persistence of Salt Precipitation to Waterfloods with Low-Salinity Brines

Further corefloods were conducted to determine the persistence of salt precipitation on permeability reduction by a conventional waterflood with a low salinity brine. The cores were initially treated with saturated brine and ethanol. For coreflood 1, the initial brine permeability was 584 mD. The core was treated with saturated brine and ethanol slugs (a total of 0.19 PV ethanol was injected) followed by shut-in of 144 hr. Coreflood 2 initially had a brine permeability of 683 mD. Coreflood 2 was treated with saturated brine, and a total of 0.31 PV of ethanol. The core was then shut-in for 65 hr. For each coreflood, an injection rate of 3 ft/d (0.9 m/d) was used. About 3 PV of saturated brine was injected followed by injection of 5% NaCl brine. A lower salinity brine (5% NaCl) was used rather than fresh water to reduce salinity shock and to prevent the possibility of clay swelling. The low-salinity brine provided a better measure of permeability changes than injection of fresh water.

Initially, for the saturated-brine injection up to 1 PV as shown in Fig. 12, the corefloods appeared to increase about 5 to 7% in permeability. One reason for this apparent increase was the displacement of alcohol which changed the fluid viscosity in the core. The permeability measured between 1 and 3 PV was probably a more accurate measure of the actual permeability. As shown
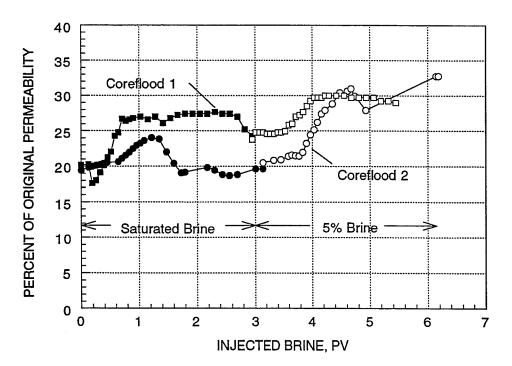

FIGURE 12. - Plot shows the persistence of permeability reduction for two corefloods. The percentage of the original permeability is shown for the injection of 3 PV of NaCl-saturated brine followed by 5% NaCl brine.

in Fig. 12, after the 5% brine injection, the permeability increased about 5% for coreflood 1 and about 10% for coreflood 2. The corefloods indicated a reasonably good persistence of salt precipitation to the injection of lower salinity brines.

Waterflooding Experiments with Parallel Cores

Experimental Conditions and Procedures

Waterflooding experiments were conducted with high- and low-permeability cores in parallel to demonstrate profile modification using alcohol-induced salt precipitation. Berea sandstone cores were used for these experiments except parallel core test 1 where a 200 to 325 mesh sandpack was used to obtain a larger permeability contrast. Permeability contrasts between high- and low-permeability cores ranged from 3 to 10. The cores were about 28 cm in length with a diameter of 3.8 cm. Table 2 shows a further description of core dimensions and properties.

All experiments were conducted at room temperature (22° C), and the cores were initially saturated with NaCl-saturated brine. With the core and coreholder mounted vertically, oil was injected into the top inlet until the oil-water ratio was 50 or greater. Crude oil from Hepler (Kansas) oil field was used for the parallel coreflood experiments. Oil from Hepler field had a viscosity of 67 cP at 22° C.

After oil saturation, high- and low-permeability cores connected in parallel were waterflooded with NaCl-saturated brine. The purpose of the initial waterflooding step was to reduce oil saturation to represent a reservoir with a watered-out channel in the high-permeability layer. For parallel core test 1 with a permeability ratio of 10, the injection rate was 1.3 ft/d (0.4 m/d). Waterflooding was continued until a water-oil ratio of 20 was reached. Also, the fluid production ratio between the high- and low-permeability cores increased from 20 to 100. Initial oil recovery of OOIP was 36% from the sandpack and 7% from the lower permeability core or 27% of the OOIP. After the initial waterflood, ethanol was injected as two equal slugs for a total of 0.046 PV. Each alcohol slug was alternated by the same slug size of NaCl-saturated brine, and the cores were shut-in several days to allow for salt crystallization. Then brine was injected at about 0.6 ft/d (0.18 m/d) to determine the effect of salt precipitation on oil recovery. Figure 13 shows oil production and water-oil-ratio history for parallel core test 1. The permeability ratios for parallel core tests 2 and 3 were 3.3 and 5.0. Since the brine permeability ratios were lower, initial waterflooding was discontinued when the water-oil ratio from the high-permeability core reached 20. The same experimental procedures were followed except ethanol was injected as three slugs. An injection rate of about 1 ft/d (0.305 m/d) was used for waterflooding and about 1.3 ft/d (0.40 m/d) for ethanol injection for these two experiments. The volume of ethanol injected for parallel core tests 2 and 3 was 0.064 and 0.088 PV, respectively. Further details of oil saturations

and injection rates are listed in Table 2. Figures 14 and 15 show oil production and water-oil history for parallel core tests 2 and 3.

Results of Parallel Core Waterflooding

As shown in Fig. 13, after ethanol treatment, the water-oil ratio decreased sharply for parallel core test 1 from about 15 to 1. Alcohol-induced salt precipitation improved in oil recovery from 7 to 42% of the oil present in the low-permeability core. This was 12% of OOIP additional oil production when the experiment was terminated at a water-oil-ratio of 15.

Parallel core tests 2 and 3 (Figs. 14 and 15) also showed that alcohol-induced salt precipitation resulted in permeability modification and improved sweep efficiency. For parallel core test 2, oil recovered from the low-permeability core increased from 11 to 42% or an additional increase of 18% of the OOIP. Figure 15 also shows a sharp decline in the water-oil-ratio after alcohol injection, and salt precipitation resulted in 16% additional recovery of the OOIP.

The fluid production ratio shown in Fig. 16 indicated that at least 90% of the injected fluid flowed into the high-permeability core during ethanol injection. Therefore, a larger fraction of injected alcohol entered into the high-permeability core which resulted in greater salt precipitation and a significant permeability reduction in the more permeable core. After salt precipitation (Fig. 16), a substantial amount of the injected fluid was diverted from the high-permeability core to the low-permeability core. After alcohol injection, the fluid production ratio between the high- and low-permeability cores was reduced from about 100 to 0.5. Fluid production ratios changed from 10 to 1 for parallel core test 2, and from 23 to 0.5 for parallel core test 3. Also, the injection pressure increased from about 2.7 psi (18.6 kPa) to 20 psi (138 kPa), and from 2.6 psi (17.9 kPa) to 30 psi (207 kPa) for parallel core tests 2 and 3.

The greater permeability modification in the high-permeability core resulted in fluid diversion into the low-permeability core and improvement in system sweep efficiency. Before water breakthrough in the low-permeability core, fluid diversion caused a water-oil ratio reduction of less than 1 for the three parallel core experiments.

TABLE 2

Core and Alcohol Injection Data for Parallel Core Experiments

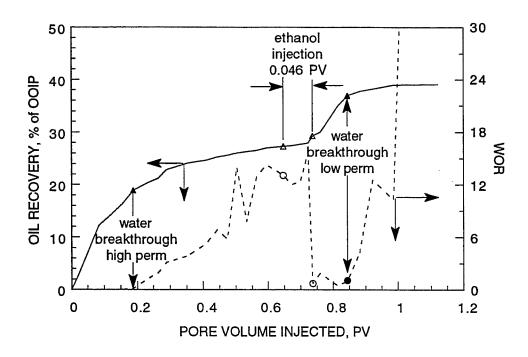| Parallel Core Test Number	Test 1		Test 2		Test 3	
	Permeability		Permeability		Permeability	
	high	low	high	low	high	low
Core type	Sandpack	Berea	Berea	Berea	Berea	Berea
Core length, cm	27.3	29.3	26.7	29.1	26.7	26.8
Porosity, %	35.4	19.2	23.3	19.2	23.0	18.9
Permeability, mD	2950	300	1130	340	730	145
Pore volume, mL	110.5	64.6	70.7	64.2	70.2	57.6
Original oil-in-place, mL	92.4	40.5	47.0	41.2	48.6	38.0
Initial oil saturation, %	83.6	62.8	66.5	64.2	69.2	66.0
Oil saturation after initial waterflood, %	47.4	55.7	23.1	52.7	26.8	55.5
Oil saturation after salt precipitation and waterflood, %	45.9	20.4	17.1	22.0	26.0	19.9
Parallel cores total PV, mL	175.1		134.9		127.8	
Permeability contrast	≈10		≈3		≈5	
Number of ethanol slugs	2		3		3	
Ethanol injection total volume (% of PV)	4.6		6.4		8.8	
injection rate, ft./D (m/d) before alcohol alcohol slug after alcohol	1.27 (0.39) 1.91 (0.58) 0.64 (0.20)		0.93 (0.28) 1.25 (0.38) 0.93 (0.28)		0.99 (0.30) 1.31 (0.40) 0.99 (0.30)	

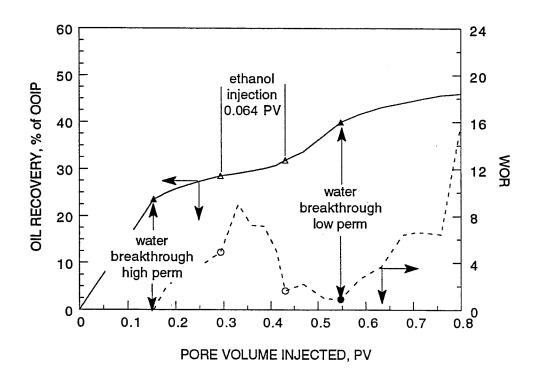FIGURE 13. - Production history for parallel core test 1.

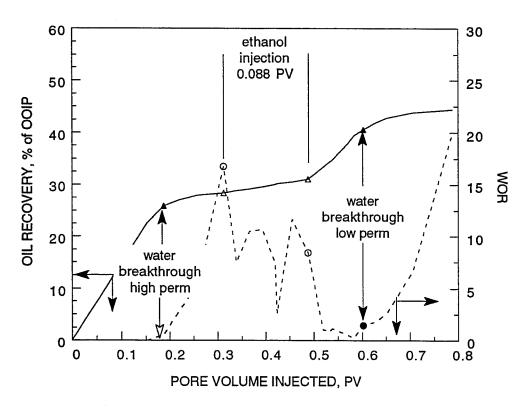FIGURE 14. - Production history for parallel core test 2.

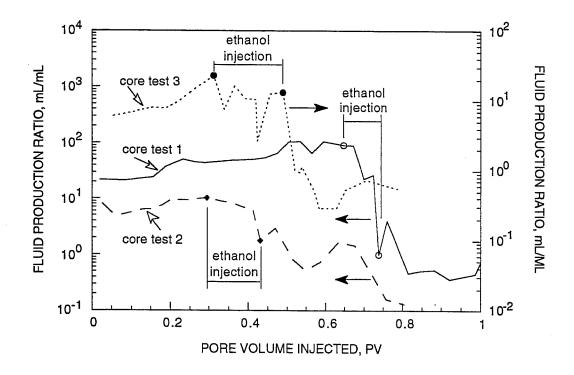FIGURE 15. - Production history for parallel core test 3.

FIGURE 16. - Fluid production ratio of high- to low-permeability cores for parallel core tests 1 to 3.

Oil Recovery with Salt Precipitation and CO₂ Displacement

Experimental Conditions and Procedures

Gas floods with CO_2 were performed to test oil recovery of alcohol-induced salt precipitation. The Berea core used in these experiments was 5.1 cm in diameter with a length of 56.2 cm. The core had a porosity of 22%. Prior to gas injection, the brine-saturated core was flooded with North Burbank crude oil with a 39.5° API gravity. Following oil saturation, the core was flooded with brine to obtain a core with a watered-out oil saturation. Coreflooding conditions were at a temperature of 65° C and a pressure of 1,200 psi (8.28 MPa). At these conditions, CO_2 was not miscible with the crude oil. A series of tests were conducted on the same core. After each test, the cores were cleaned and flushed with a series of solvents including Stoddard solvent, normal propyl alcohol, acetone, and brine.

For comparison of oil recovery, two CO_2 floods were conducted without salt precipitation or ethanol injection. Because ethanol was used in the salt precipitation method, a CO_2 displacement test was conducted to determine if ethanol injection without salt precipitation resulted in additional produced oil. For the ethanol injection test, two 0.075 PV (19 cm³) slugs of ethanol were injected. Each ethanol slug was chased with an equal volume of 2% KCl. A low-concentration brine was used to minimize salt precipitation, and KCl was used to reduce swelling of clays in the core.

Another CO_2 flood was made to test the effect of salt precipitation on oil recovery. A 10% NaCl brine was used for core saturation and flooding. Two 10.5-cm^3 slugs of ethanol were injected for the salt precipitation experiment. The total quantity of ethanol was 0.083 PV. Each ethanol slug was followed by an equal volume of NaCl-saturated brine. A small quantity of fresh water (1.8 cm^3) was injected preceding each brine and alcohol injection to reduce precipitation of salt in the core inlet and injection tubing. This was accomplished by inserting a 1.8-cm^3 loop filled with fresh water between the core inlet and brine or alcohol injection. Following brine and alcohol injection, the core was shut-in for 5 days to allow for salt crystal growth and increased crystal size prior to initiating the CO_2 flood.

Results of Coreflooding Tests with CO_2

The results of oil recoveries for CO_2 floods are shown in Table 3. Comparison of these results with and without salt precipitation indicated the quantity of produced oil was approximately 40% higher or about 12% additional recovery of the OOIP. Also, to a lesser extent, some additional oil recovery was indicated for the alcohol injection flood. The alcohol, necessary to induce salt precipitation, probably was partially responsible for increased oil recovery. The mechanisms for the increased oil recovery may be due to several factors. Alcohol may reduce interfacial tension between the brine and oil resulting in greater oil mobilization and higher oil production. Also, precipitated salt partially plugged the more permeable channels in the watered-out core. This diverted subsequent CO_2 flooding to less permeable areas of the core with higher oil saturation, thereby improving sweep efficiency and increasing oil production.

TABLE 3

Comparison of Oil Recovery for CO_2 Floods and
CO_2 Floods with Ethanol Injection and Salt Precipitation

Coreflood Test	Original oil in core mL	Oil remaining after CO_2 flood		Produced oil	
		mL	%	mL	%
CO_2 flood	111.0	77.1	69.5	33.9	30.5
CO_2 flood with 0.083 PV ethanol and NaCl saturated brine	109.5	64.5	58.9	45.0	41.1
CO_2 flood with 0.12 PV ethanol	105.4	67.5	64.4	37.5	35.6
CO_2 flood	108.4	79.4	73.2	29.0	26.8

These experiments were conducted with relatively high-permeability (500 mD) and homogeneous Berea core. Only a limited number of tests were performed, and further experiments are necessary to confirm these results. However, greater oil recovery was indicated by the salt precipitation method. Profile modification with improved sweep efficiency was indicated even in this core with relatively uniform permeability. Previously, as stated in this report, waterflooding experiments showed profile modification and fluid flow diversion were achieved in parallel cores. Even greater sweep efficiency and higher oil production may be possible for this method with CO_2 floods in nonuniform or layered rocks with contrasting permeabilities.

CONCLUSIONS

1. Ethanol is the most effective alcohol for inducing salt precipitation. Methanol could also be used if the cost was sufficiently low to offset the higher salt solubility and lower quantity of salt precipitation from brine and methanol mixtures. NaCl was used for this method because of the lower solubility in alcohol/brine mixtures, low cost, and availability. Both NaCl and ethanol are non toxic compounds which are environmentally acceptable for oil well injection.

2. In parallel coreflooding experiments, the injection of alcohol and NaCl saturated brine selectively reduced the permeability in the high-permeability core. After initial waterflooding, the higher relative permeability to brine and alcohol resulted in proportionately more alcohol and brine flow into the high-permeability core. This resulted in more salt precipitation and greater plugging of the high-permeability core.

3. The low viscosity of brine and alcohol should minimize viscous crossflow during injection. Because of limited crossflow during injection, there will be better penetration and placement in the higher permeability or thief zones.

4. The salt precipitation method should not be affected by adsorption, and reservoir conditions such as temperature and pH. These conditions can adversely affect other profile modification methods such as gelled polymers.

5. Cores with permeabilities modified by salt precipitation were resistant to subsequent waterfloods with low-salinity brine. After several PV of low-salinity brine injection, the core permeabilities recovered only 5 to 10% of the original permeability.

6. Using 6.4 to 8.8% PV of ethanol injection for salt precipitation, waterflood experiments with high- and low-permeability parallel cores increased oil recovery by about 17% of the OOIP or about 60% more oil recovery over conventional waterflooding. Modified flow profiles were largely responsible for the increase in oil recovery.

7. Salt precipitation increased oil recovery for an immiscible CO_2 flood. Ethanol used in the salt precipitation method was partially responsible for the increased oil recovery. However, more oil was recovered with the salt precipitation experiment.

ACKNOWLEDGMENTS

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